

AD-A080 091

VERMONT UNIV BURLINGTON DEPT OF CHEMISTRY  
ORGANOPHOSPHAZENES. XIV. PARA SUBSTITUTED ARYL AND MIXED PARA S--ETC(U)  
JAN 80 C W ALLEN, G E BRUNST, M E PERLMAN

F/G 7/3

N00014-77-C-0605

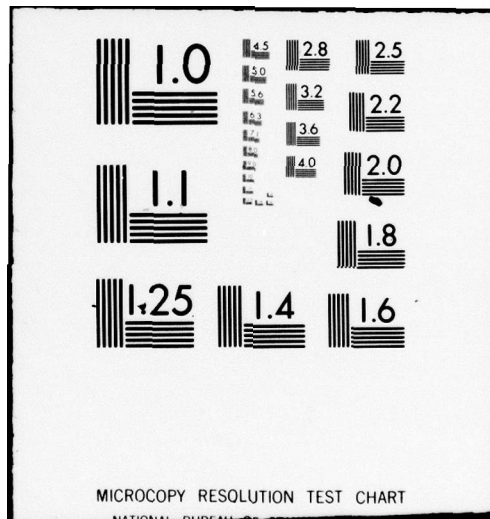
UNCLASSIFIED

TR-6

NL

| OF |  
AD A  
080091





ADA 080091

AD75-218

DNC FILE COPY

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

REPORT DOCUMENTATION PAGE

READ INSTRUCTIONS  
BEFORE COMPLETING FORM

1. REPORT NUMBER 6	2. GOVT ACCESSION NO.	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) Organophosphazenes. XIV. Para Substituted Aryl and Mixed Para Substituted Aryl/Phenyl Fluorocyclotriphosphazenes		5. TYPE OF REPORT & PERIOD COVERED Technical Report
7. AUTHOR(s) Christopher W. Allen, George E. Brunst and Michael E. Perlman		6. PERFORMING ORG. REPORT NUMBER
9. PERFORMING ORGANIZATION NAME AND ADDRESS Department of Chemistry University of Vermont Burlington, Vermont 05405		8. CONTRACT OR GRANT NUMBER(s) N0001477C-0605
11. CONTROLLING OFFICE NAME AND ADDRESS Department of the NAVY Office of Naval Research Arlington, VA 22217		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)		12. REPORT DATE January 15, 1980
		13. NUMBER OF PAGES 16
		15. SECURITY CLASS. (of this report) Unclassified
		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE
16. DISTRIBUTION STATEMENT (of this Report) Approved for public release and sale; its distribution is unlimited		
17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)		
18. SUPPLEMENTARY NOTES Submitted for publication in Inorganica Chemica Acta		
19. KEY WORDS (Continue on reverse side if necessary and identify by block number) Phosphazenes Aryl Derivatives Mass Spectrometry NMR Spectroscopy Aryl lithium reagents		
20. ABSTRACT (Continue on reverse side if necessary and identify by block number) The reactions of aryl lithium reagents containing electron donating substituents in the para position with hexafluorocyclotriphosphazene, $P_3N_3F_6$ , have been examined. These reactions yield the appropriate monoaryl penta- fluorocyclotriphosphazenes, $P_3N_3F_5C_6H_4X$ ( $X=F, Cl, OCH_3, CH_3$ ) in moderate yields. The monoaryl phosphazenes are converted to the geminally substituted mixed aryl/phenyl derivatives, $2,2-P_3N_3F_4(C_6H_5)C_6H_4X$ ( $X=F, Cl, OCH_3, CH_3$ ), by the Friedel-Crafts reaction. The infrared and nmr spectroscopic data		

DDC  
RECEIVED  
JAN 30 1980  
A

DD FORM 1 JAN 73 1473

EDITION OF 1 NOV 63 IS OBSOLETE  
S/N 0102-014-6601

408892  
SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

20. (cont.)

along with the mass spectrometry data are discussed in terms of perturbations of the aryl system by both the phosphazene and electron donor substituents.



14 TR-6

OFFICE OF NAVAL RESEARCH

Contract N0001477C-0605

Project NR 356-663

9 Technical Report No. 6

6

Organophosphazenes. XIV. Para Substituted  
Aryl and Mixed Para Substituted Aryl/ Phenyl  
Fluorocyclotriphosphazene Derivatives,

by

10

Christopher W. Allen, George E. Brunst and  
Michael E. Perlman

Prepared for Publication in  
Inorganica Chimica Acta

15

N00014-77-C-0605

University of Vermont  
Department of Chemistry  
Burlington, Vermont 05405

11 15 Jan 80

12

21

Accession For	
NTIS GRA&I	<input checked="" type="checkbox"/>
DDC TAB	<input type="checkbox"/>
Unannounced	<input type="checkbox"/>
Justification	
By _____	
Distribution/	
Availability Codes	
Dist.	Avail and/or special
A	

Reproduction in whole or in part is permitted  
for any purposes of the United States Government.

This document has been approved for public release  
and sale; its distribution is unlimited.

408 892

AB

80

1

28

045

**Organophosphazenes. XIV. Para Substituted Aryl and Mixed Para  
Substituted Aryl/Phenyl Fluorocyclotriphosphazene Derivatives.<sup>1</sup>**

**Christopher W. Allen\*, George E. Brunst and  
Michael E. Perlman**

**Department of Chemistry  
University of Vermont  
Burlington, Vermont 05405, USA**

The reactions of aryl lithium reagents containing electron donating substituents in the para position with hexafluorocyclotriphosphazene,  $P_3N_3F_6$ , have been examined. These reactions yield the appropriate monoaryl pentafluorocyclotriphosphazenes,  $P_3N_3F_5C_6H_4X$  ( $X = F, Cl, OCH_3, CH_3$ ) in moderate yields. The monoaryl phosphazenes are converted to the geminally substituted mixed aryl/phenyl derivatives,  $2,2-P_3N_3F_4(C_6H_5)C_6H_4X$  ( $X = F, Cl, OCH_3, CH_3$ ), by the Friedel-Crafts reaction. The infrared and nmr spectroscopic data along with the mass spectrometry data are discussed in terms of perturbations of the aryl system by both the phosphazene and electron donor substituents.

## Introduction

The reactions of aryl lithium reagents with cyclic<sup>1-4</sup> and polymeric phosphazenes<sup>5</sup> have proved to be of value for the preparation of aryl-phosphazenes. To date phenyl,<sup>2,3</sup> tolyl,<sup>2,3</sup> p-dimethylaminophenyl,<sup>1</sup> fluorophenyl<sup>4</sup> and perfluorophenyl<sup>4</sup> derivatives have been synthesized. In addition to aryl species, a wide variety of other organolithium reagents have been shown to undergo reactions with cyclophosphazenes.<sup>6-11</sup> This investigation involves the extension of this synthetic technique to the preparation of aryl phosphazenes with a variety of electron donating functional groups in the para position of the aryl ring. Interest in this type of compound is related to two topics of continuing interest in our studies of organophosphazenes. We have previously shown that the p-dimethylaminophenyl group functions as an effective electron donor to the strongly electron accepting fluorophosphazene moiety.<sup>12</sup> Consequently, it was of interest to prepare aryl phosphazenes with a range of electron donating groups on the aryl ring in order to probe the manifestations of these electronic effects on basic spectroscopic properties. We also have been developing organofunctional phosphazenes in order to provide starting materials for the preparation of new organophosphazenes via synthetic transformations of the exocyclic group.<sup>10,11,13</sup> Organofunctional arylphosphazenes would provide another possible source to new organophosphazenes.

## Experimental

Materials and Measurements Hexachlorocyclotriphosphazene (Ethyl Corp.) was converted to hexafluorocyclophosphazene ( $P_3N_3F_6$ )<sup>14</sup> which in turn was converted to paratolylpentafluorocyclotriphosphazene<sup>2</sup> by previously reported procedures. Benzene<sup>15</sup> and diethylether were distilled over sodium. Triethylamine was distilled from potassium hydroxide. The following reagents were used without

further purification: n-butyl lithium (Alfa), 1-bromo-4-chlorobenzene (Adrich), 1-bromo-4-fluorobenzene and 4-bromo-anisole (Eastman Kodak). Nmr Spectra were obtained on a JEOL C-60HL spectrophotometer as fifteen percent cyclohexane solutions. Further dilutions did not produce any change in chemical shifts.<sup>16</sup> Second order spectra simulated with the LACON III Program. Infrared spectra were obtained on thin films or nujol mulls using a Beckman IR-20A spectrophotometer with sodium chloride disks and were calibrated with polystyrene bands. Mass spectra were obtained on a Perkin-Elmer RMU-6D spectrophotometer at 80eV. In certain cases ionizing volt ages were varied from 80 to 15 eV with the lower limit taken as approaching the appearance potential. Calibration was accomplished using perfluorokerosene. Elemental analyses were performed by the Robertson Laboratories.

Preparation of Mono (p-fluorophenyl)pentafluorocyclotriphosphazene. The procedure discussed here is a modification of those reported for the preparation of phenyl<sup>3</sup> and p-fluorophenyl fluorocyclotriphosphazenes.<sup>4</sup> A three-necked round-bottomed flask charged with 200 ml of diethyl ether, a stirring bar and 6.88 ml (0.06 mole) of  $p\text{-FC}_6\text{H}_4\text{Br}$  was fitted with a nitrogen inlet, a pressure-equalizing dropping funnel and a reflux condenser attached to a mercury bubbler. The flask was cooled to  $-78^\circ$  and flushed with nitrogen for 10 min. A solution of n-butyl lithium in hexane (25 ml, 0.06 mole) was admitted to the dropping funnel through a septum cup with a syringe. The butyl lithium solution was added to the  $p\text{-FC}_6\text{H}_4\text{Br}$  solution dropwise over a period of 30 min with constant stirring. The solution was allowed to come to room temperature and stirring was continued for 45 minutes. A second three-necked flask was charged with a solution of 15.0 g (0.06 mole) of  $\text{P}_3\text{N}_3\text{F}_6$  in 70 ml of diethyl ether and fitted with a nitrogen inlet and a reflux condenser attached to a mercury bubbler. An angled tube with 24/40 outer joints at each end was fitted to a pressure-equalizing

dropping funnel at one end while the other end replaced the reflux condenser on the flask containing the  $p\text{-FC}_6\text{H}_4\text{Li}$  solution, thus allowing transfer of the organometallic reagent. The dropping funnel was fitted to the flask containing the phosphazene solution. The assembled system was flushed with nitrogen at  $-78^\circ$  and then the  $p\text{-FC}_6\text{H}_4\text{Li}$  solution was added at  $0^\circ$  over a period of 90 min. The mixture was allowed to stir for an additional 2 hours at room temperature. After the solvent was removed, 100 ml of medium boiling petroleum ether was added and the solution was stored overnight at  $10^\circ$ . Repeated filtrations through filter aid were required to remove all of the lithium halides. The clear solution was treated with activated carbon. After removal of the carbon and solvent, the oily residue was distilled through a vigreux column at 0.6 mm, and the fractions boiling at  $66\text{--}68^\circ$  were collected; yield 6.2g (32% of theory<sup>17</sup>) of a water white liquid. Anal. Calcd for  $\text{P}_3\text{N}_3\text{F}_5\text{C}_6\text{H}_4\text{F}$ : C, 22.17; H, 1.24; mol wt, 325. Found: C, 22.26; H, 1.32; mol wt, 325 (mass spectrum).

Using procedures identical to those described above, para substituted monoaryl pentafluorocyclophosphazenes with the formulae  $\text{P}_3\text{N}_3\text{F}_5\text{C}_6\text{H}_4\text{X}$  ( $\text{X} = \text{Cl}$ ,  $\text{OCH}_3$ ) were prepared. These compounds were identified by ir and nmr spectroscopy and mass spectrometry.

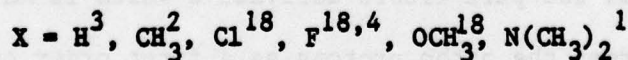
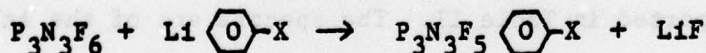
Preparation of Geminal (p-methoxyphenyl)(phenyl) tetrafluorocyclotriphosphazene. In a typical reaction, 20 ml of benzene<sup>15</sup> was distilled into a 50 ml, three-necked, round-bottomed flask containing 1.04 ml (0.007 mole) of triethylamine and a stirring bar. The flask was charged with 6.0 g (0.023 mole) of aluminum chloride and fitted with a reflux condenser attached to a mercury bubbler and a pressure-equalizing funnel containing 1.9 g (0.005 mole) of  $\text{P}_3\text{N}_3\text{F}_5\text{C}_6\text{H}_4\text{OCH}_3$  in 5 ml of freshly distilled benzene. The flask was heated to reflux with constant stirring. After 30 minutes, the  $\text{P}_3\text{N}_3\text{F}_5\text{C}_6\text{H}_4\text{OCH}_3$  solution was added dropwise. The reaction was allowed to continue for 24 hours. After allowing the reaction mixture to cool, it was poured into a 150 ml beaker

which was one-third filled with cracked ice and contained 0.5 ml of concentrated hydrochloric acid. The layers were separated and the water layer was extracted with benzene.<sup>15</sup> The benzene layers were combined, extracted with water, aqueous sodium bicarbonate and water. The benzene layer was then dried over magnesium sulfate and treated with activated carbon. The solids and solvent were successively removed and the resulting oil was heated in a sublimation apparatus at 150° and 0.5 mm. A white crystalline solid, 1.1 g (53% of theory), mp 102-103° was obtained. Anal. Calcd for  $P_3N_3F_4(C_6H_5)C_6H_4OCH_3$ : C, 39.49; H, 3.03; mol wt 395. Found: C, 37.53; H, 2.95; mol wt 395 (mass spectrum).

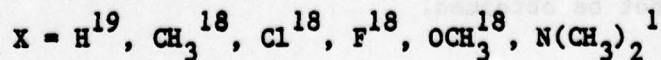
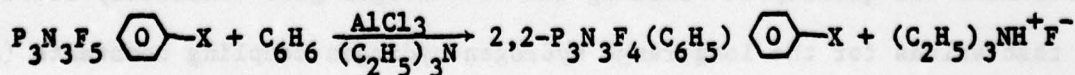
Using procedures identical to those described above, mixed phenyl, parasubstituted aryl tetrafluorophosphazenes with the formulae  $2,2-P_3N_3F_4(C_6H_5)-C_6H_4X$  ( $X = CH_3, F, Cl$ ) were prepared. These compounds were identified by ir and nmr spectroscopy, and mass spectrometry.

#### Results and Discussion

This investigation, when combined with previous investigations, demonstrates the broad scope of the organolithium reaction for the preparation of monoaryl-



pentafluorocyclotriphosphazenes. Furthermore, all of these species may effectively converted to the mixed phenyl/aryl tetrafluorocyclotriphosphazenes via the Friedel-Crafts reaction.



Thus, the organolithium reaction represents a good route to the synthesis of

arylphosphazenes with electron donating substituents on the aryl ring. Since aryl lithium reagents with electron withdrawing substituents are only stable at significantly reduced temperatures<sup>20</sup>, aryl phosphazenes with electron withdrawing substituents are expected to be difficult to prepare.

The infrared spectra of the aryl fluorocyclotriphosphazenes are reported in Table I. The  $\nu_{\text{NPN}}$  ring vibration of the monosubstituted phosphazenes occurs between  $1260\text{--}1263\text{ cm}^{-1}$ . The replacement of a fluorine atom by a phenyl group leads to decrease of  $8\text{--}10\text{ cm}^{-1}$  in  $\nu_{\text{NPN}}$ . It is of interest to observe that a variation of para substituents on the aryl ring produces small variations in the phosphazene ring vibrational frequency. A further discussion of the origin of this effect is not warranted due to broad band width (even after successive dilution) and the complex nature of the transmission of aryl electronic effects to the phosphazene<sup>12</sup>. The magnitude of the decrease in  $\nu_{\text{NPN}}$  on going to the disubstituted derivative is consistent with geminal rather than non-geminal substitution<sup>19</sup>. The geminal nature of the disubstituted derivative may also be demonstrated by the absence of a strong band which occurs in the region of  $760\text{ cm}^{-1}$  in non-geminal phenylfluorocyclotriphosphazenes.<sup>21</sup>

The  $^1\text{H}$  nmr data for the aryl protons of the monoaryl pentafluorocyclotriphosphazenes is reported in Table II. The spectra are of the  $\text{AA}'\text{BB}'\text{X}$  type (with the exception of the para fluoro derivative which is  $\text{AA}'\text{BB}'\text{MX}$ ). Although it was tempting to treat the ortho protons as a first order case, it was found that simulation of the spectra using the LACON III program was necessary in order to obtain a consistent set of parameters. A combination of unresolved resonances and quadrupole broadening due to nitrogen gave relatively broad lines so that values for the long range hydrogen-hydrogen coupling constants ( $J_{\text{HoHo}}$  and  $J_{\text{HmHm}}$ ) could not be obtained.

The chemical shifts of the protons ortho to the phosphazene ring are essentially constant for the para substituent being  $\text{CH}_3$ , Cl or  $\text{OCH}_3$ . Since the geometry of the system stays constant through the series, the ortho shifts are controlled by a combination of the anisotropic and electronic effects of the phosphazene ring. The ortho shift for the para fluoro derivative is significantly removed from the others in the series suggesting a stronger involvement of the para substituent in perturbation of the aryl ring electronic structure in this case. In para disubstituted benzene derivatives, one generally observes that the combination of a strong electron donor and strong electron acceptor produces a large difference in the ortho and meta chemical shifts ( $\Delta\text{om}$ ) while in cases where the discrimination between the groups is less dramatic, the value of  $\Delta\text{om}$  is smaller. In the molecules under consideration in this investigation, the strongly electron withdrawing effect of the pentafluorocyclotriphosphazene moiety<sup>12,16,22</sup> combined with good  $\pi$  donors (e.g. F,  $\text{OCH}_3$ ) results in significantly larger values of  $\Delta\text{om}$  than when the phosphazene is combined with weak electron donors (e.g.  $\text{CH}_3$ , Cl). The phosphorus-ortho hydrogen coupling constant ( $J_{\text{PHo}}$ ) is of the same order of magnitude as previously reported for aryl phosphorus (v) compounds.<sup>16,23</sup> The better  $\pi$  donors (F,  $\text{OCH}_3$ ) exhibit lower coupling constants while the poorer electron donors (Cl,  $\text{CH}_3$ ) exhibit higher values of  $J_{\text{PHo}}$ . The more electron density in the aryl ring, the lower the effective charge on the ortho hydrogen atom and hence one observes a reduction in the value of  $J_{\text{PHo}}$ . In keeping with previous observations<sup>24</sup>, the small variation in the hydrogen-hydrogen coupling constant,  $J_{\text{HoHm}}$ , is related to the substituent group electronegativity values.

The mass spectra for the monoaryl pentafluorocyclotriphosphazenes are reported on Table III. The basic fragmentation process observed is the same as previously established for the monophenyl derivative.<sup>25</sup> This consistency throughout a series of compounds is important in the application of mass

spectrometry to the identification of new compounds. Features which are unique to individual molecules can usually be related to the known fragmentation tendencies of the organic moiety e.g. loss of the methyl group in the para methoxy derivative and tropyllium ion formation in the para tolyl derivative.

The mass spectra of the mixed aryl/phenyl tetrafluorocyclotriphosphazenes (Table IV) are also understandable in terms of the basic process established for phenyl fluorocyclotriphosphazenes<sup>25</sup> with perturbations reflecting para substituent fragmentation. Organic group substituent decomposition makes significant contributions to the mass spectra of the diorgano derivatives, particularly in the para methoxyl and tolyl derivatives. The basic phosphazene fragmentation route observed is the successive cleavage of the aryl groups which is characteristic of geminally substituted derivatives.<sup>25</sup> Thus, the mass spectrometry data confirm the infrared results in the assignment of the geminal configuration to the disubstituted derivatives (the expected product in a Friedel-Crafts reaction<sup>19</sup>). It is of particular interest to compare the intensity of the ion resulting from the loss of the phenyl group ( $P_3N_3F_4C_6H_4X^+$ ) compared to the ion resulting from the loss of the para substituted aryl group ( $P_3N_3F_4C_6H_5^+$ ). Previously, we have shown that a phenyl group is lost in preference to a para dimethylaminophenyl group in geminal phenyl/para-dimethylaminophenyl fluorocyclotriphazenes and this observation was attributed to higher bond strength in the phosphorus-paradimethylaminophenyl unit than in the phosphorus-phenyl bond.<sup>25</sup> The tendency to lose a phenyl group in preference to the aryl group with an electron donating substituent is observed in most of the mixed aryl/phenyl derivatives in this investigation. The apparent reversal of this trend in the para chloro derivative relates to the fact that there are two possible precursors to the  $P_3N_3F_4C_6H_5^+$  ion i.e.  $P_3N_3F_4(C_6H_5)C_6H_4Cl^+$  and  $P_3N_3(C_6H_5)C_6H_4^+$ . The mass spectrum of  $P_3N_3F_4(C_6H_5)-C_6H_4CH_3$  is rather complex with no  $P_3N_3F_4C_6H_5^+$  ion and a very intense ion

associated with tropyllium derivative. In order to insure that the observed intensity differences are related to thermodynamic parameters, the spectra of the two derivatives with strong electron donors (fluoro and methoxy) were run at successively lower ionization energies until the region approaching the appearance potential was reached (approximately 15 to 18eV). In the para methoxyl derivative the intensity difference between the  $P_3N_3F_4C_6H_5O^+$  and the  $P_3N_3F_4C_6H_5^+$  ions increases at lower ionization energies. While in the case of the para fluoro derivative, the ratio of the  $P_3N_3F_4C_6H_4F^+$  to the  $P_3N_3F_5C_6H_5^+$  ion intensities approaches unity at lower ionization energies. Thus in the paramethoxy case, phosphorus-carbon bond enthalpy is greater in the bond to the para substituted aryl group. In the para fluoro derivative, there is no preferential phosphorus-carbon stabilization in the appearance potential region consequently the intensity difference at higher ionization energies is related to kinetic effects. Two of most probable kinetic effects which are reasonable for this system are stabilization of the developing positive ion by the electron donating para-fluorophenyl moiety and the superior leaving group ability of the phenyl group.

Acknowledgment. This work was supported, in part, by the Office of Naval Research.

References and Notes  
~~~~~


1. Part XIII: C. W. Allen and P. L. Toch, submitted to Inorg. Chem.
2. T. Moeller and F. Tsang, Chem. Ind. (London), 361 (1962).
3. C. W. Allen and T. Moeller, Inorg. Chem., 7, 2177 (1968).
4. T. Chievers and N. L. Paddock, Inorg. Chem., 11, 848 (1972).
5. H. R. Allcock, Acc. Chem. Res., 12, 351 (1979); H. R. Allcock and C. T-W. Chu, Macromolecules, 12, 551 (1979).
6. T. Moeller, A. Failli and F. Y. Tsang, Inorg. Nucl. Chem. Letters, 1, 49 (1969)
7. E. Niecke, H. Thamm, O. Glemser, Z. Naturforsch., 26b, 366 (1971).
8. T. N. Ranganathan, S. M. Todd, and N. L. Paddock, Inorg. Chem., 12, 316 (1973).
9. T. Chievers, Inorg. Nucl. Chem. Letters, 7, 827 (1971).
10. J. G. Dupont and C. W. Allen, Inorg. Chem., 16, 2694 (1977).
11. J. G. Dupont and C. W. Allen, Inorg. Chem., 17, 3093 (1978).
12. C. W. Allen and J. C. Green, Inorg. Chem., in press.
13. J. G. Dupont and C. W. Allen, Macromolecules, 12, 169 (1979).
14. T. Moeller, K. John and F. Tsang, Chem. Ind. (London), 347 (1961).
15. Benzene is a cancer suspect agent and hence all manipulations involving benzene should be done in a fume hood and utilizing appropriate precautions.
16. C. W. Allen and A. J. White, Inorg. Chem., 13, 1220 (1974).
17. literature value for the yield of  $P_3N_3F_5C_6H_4F$  is 14%.
18. This investigation
19. C. W. Allen, F. Y. Tang and T. Moeller, Inorg. Chem., 7, 2183 (1968).
20. G. Köbrich and P. Buck, Chem. Ber., 103, 1412 (1970).
21. This band is reported in the solution ir spectra of non-geminal phenyl fluorophosphazenes<sup>3</sup> however it also occurs in mull spectra.
22. C. W. Allen, J. Organometal. Chem., 125, 215 (1977).

23. C. E. Griffin, Tetrahedron, 20, 2399 (1964); C. E. Griffin, J. J. Burke, F. E. Dickson, M. Gordon, H. H. Hsieh, R. Obrycki and M. P. Williamson, J. Phys. Chem., 71, 4458 (1967); C. E. Griffin, R. B. Davidson and M. Gordon, Tetrahedron, 22, 561 (1966).
24. S. Castellano and W. G. Schneider, J. Chem. Phys., 35, 731 (1961).
25. C. W. Allen and P. L. Toch, J. C. S. Dalton, 1685 (1974).


TABLE I. Selected IR Data<sup>a</sup>

| Compound                                                                              | $\nu_{\text{NPN}}$ | $\nu_{\text{PF asym}}$ | $\nu_{\text{PF sym}}$ |                                                         |
|---------------------------------------------------------------------------------------|--------------------|------------------------|-----------------------|---------------------------------------------------------|
| $\text{P}_3\text{N}_3\text{F}_5\text{C}_6\text{H}_4\text{F}$                          | 1263vs             | 1238s                  | 938vs                 | 853s, 822vs<br>793ms, 726ms, 723s<br>709m<br>728m, 719w |
| $\text{P}_3\text{N}_3\text{F}_4(\text{C}_6\text{H}_5)\text{C}_6\text{H}_4\text{F}$    | 1254vs             | 1234s                  | 922s, 900m            | 814s                                                    |
| $\text{P}_3\text{N}_3\text{F}_5\text{C}_6\text{H}_4\text{CH}_3$                       | 1262vs             | 977s                   | 941vs                 | 857s, 830vs                                             |
| $\text{P}_3\text{N}_3\text{F}_4(\text{C}_6\text{H}_5)\text{C}_6\text{H}_4\text{CH}_3$ | 1252vs             | 962m                   | 953s, 910s            | 820s, 810s                                              |
| $\text{P}_3\text{N}_3\text{F}_5\text{C}_6\text{H}_4\text{OCH}_3$                      | 1260vs             |                        | 931vs                 | 846s, 822w                                              |
| $\text{P}_3\text{N}_3\text{F}_4(\text{C}_6\text{H}_5)\text{C}_6\text{H}_4\text{CH}_3$ | 1252vs             | 1217s                  | 937w, 906s            | 825m, 809ms                                             |
| $\text{P}_3\text{N}_3\text{F}_5\text{C}_6\text{H}_4\text{Cl}$                         | 1261vs             |                        | 935vs                 | 850s 832vs, 813s<br>738m                                |
| $\text{P}_3\text{N}_3\text{F}_4(\text{C}_6\text{H}_5)\text{C}_6\text{H}_4\text{Cl}$   | 1250vs             | 949w                   | 921s, 902s            | 806s<br>739ms, 727ms                                    |

a. All frequencies in  $\text{cm}^{-1}$ ; calibrated with polystyrene band at  $1601\text{-}8\text{cm}^{-1}$ .

TABLE II.  
<sup>1</sup>H NMR Data for Aryl pentafluorocyclotriphosphazenes, P<sub>3</sub>N<sub>3</sub>F<sub>5</sub>-X

| x                | δ <sub>Ho</sub> | δ <sub>Hm</sub> | Δ <sub>on</sub> | J <sub>HoHm</sub> | J <sub>PHo</sub> | J <sub>PHm</sub> |
|------------------|-----------------|-----------------|-----------------|-------------------|------------------|------------------|
| OCH <sub>3</sub> | 7.80            | 6.94            | 0.86            | 9.1               | 15.5             | 4.0              |
| F                | 7.96            | 7.17            | 0.79            | 9.0               | 15.0             | 4.0              |
| CH <sub>3</sub>  | 7.80            | 7.28            | 0.52            | 8.2               | 16.2             | 4.5              |
| Cl               | 7.82            | 7.46            | 0.36            | 8.5               | 15.7             | 3.5              |

TABLE III. Mass Spectrometry Data for Aryl pentafluoro-cyclotriphosphazenes,  $P_3N_3F_5$  -X <sup>a</sup>

| Assignment               | Relative Abundance |                   |                 |                 |
|--------------------------|--------------------|-------------------|-----------------|-----------------|
|                          | F                  | CH <sub>3</sub> O | Cl <sup>b</sup> | CH <sub>3</sub> |
| $P_3N_3F_5C_6H_4X^+$     | 100%               | 100%              | 100%            | 100%            |
| $[P_3N_3F_5C_6H_4X-H]^+$ | 1.8                | 3.0               | 2.3             | 28.5            |
| $P_3N_3F_5C_6H_4O^+$     |                    | 12.6              |                 |                 |
| $P_3N_3F_5C_6H_4^+$      | 2.6                | 4.4               | 4.1             | 1.1             |
| $P_3N_3F_5C_5H_4^+$      |                    | 19.7              |                 | 0.5             |
| m/e = 248                | 1.1                | 1.1               | 24.3            |                 |
| $P_3N_3F_5C^+$           | 5.2                | 2.8               | 6.8             | 3.5             |
| $P_3N_3F_5H^+$           | 2.3                | 2.6               | 3.6             | 2.0             |
| $P_3N_3F_5^+$            | 10.5               | 8.2               | 11.6            | 9.6             |
| $P_3N_2F_5^+$            | 34.1               | 14.2              | 50.0            | 13.2            |
| $P_3N_3F_4H^+$           | 1.3                | 1.6               | 3.9             | 2.0             |
| $P_3N_3F_4^+$            | 0.9                | 0.8               | 3.3             | 1.1             |
| $P_3N_2F_4^+$            | 4.9                | 6.8               | 4.5             | 9.8             |
| $P_2NF_5H^+$             |                    |                   |                 | 4.3             |
| $P_2NF_5^+$              | 6.8                | 6.3               | 8.2             | 8.6             |
| $P_3N_3F_5C_6H_4X^{2+}$  | 2.7                | 3.3               | 2.7             | 4.1             |
| $P_3N_3F_5C_8H_6^{2+}$   |                    |                   |                 | 6.7             |
| $P_2NF_4^+$              | 3.9                | 3.8               | 4.5             | 5.3             |
| $P_2NF_3^+$              | 1.1                | 1.2               | 1.8             | 1.7             |
| $P_2NF_2^+$              | 3.9                | 3.0               | 5.0             | 0.6             |
| $PN_2F_2^+$              | 1.7                | 4.9               | 2.3             | 2.1             |
| $NC_6H_4X^+$             | 4.6                | 2.8               | 3.6             | 5.0             |
| $C_6H_4X^+$              | 3.9                | 4.9               | 3.0             | 18.0            |

a. Obtained at 80ev    b. based on <sup>35</sup>Cl.

TABLE IV. Selected Mass Spectrometry Data for Aryl phenyl tetrafluorocyclotriphosphazenes,  $P_3N_3F_4(C_6H_5)C_6H_4X^a$

| Assignment                         | Relative Abundance |                   |                 |                              |
|------------------------------------|--------------------|-------------------|-----------------|------------------------------|
|                                    | F                  | CH <sub>3</sub> O | Cl <sup>b</sup> | CH <sub>3</sub> <sup>c</sup> |
| $[P_3N_3F_4(C_6H_5)C_6H_4X + H]^+$ | 93                 | 26                |                 |                              |
| $P_3N_3F_4(C_6H_5)C_6H_4X^+$       | 100                | 34                | 97              | 4                            |
| $[P_3N_3F_4(C_6H_5)C_6H_4X - H]^+$ |                    | 17.2              | 100             | 7                            |
| $P_3N_3F_4(C_6H_5)C_6H_5O^+$       |                    | 100               |                 |                              |
| $P_3N_3F_4(C_6H_5)C_6H_4O^+$       |                    | 100               |                 |                              |
| $P_3N_3F_4(C_6H_5)C_6H_4^+$        |                    |                   | 24.7            |                              |
| $P_3N_3F_4C_6H_4X^+$               | 31                 |                   | 39              | 52                           |
| $P_3N_3F_4C_7H_7^+$                |                    |                   |                 | 100                          |
| $P_3N_3F_4C_6H_5O^+$               |                    | 56                |                 |                              |
| $P_3N_3F_4C_6H_5^+$                | 10.5               | 18                | 48              | 0                            |
| $P_3N_3F_4^+$                      | 13.7               | 8.9               | 24.7            | 11                           |
| $P_3N_2F_4^+$                      | 8.7                | 4.3               | 32.5            | 15.2                         |

- a. Obtained at 80ev; only ions relevant to the discussion reported. b. based on <sup>35</sup>Cl  
c. complex spectrum, possibly due to impurity peaks.

# TECHNICAL REPORT DISTRIBUTION LIST, GEN

|                                                                                                                              | <u>No.</u><br><u>Copies</u> |                                                                                                                                     | <u>No.</u><br><u>Copies</u> |
|------------------------------------------------------------------------------------------------------------------------------|-----------------------------|-------------------------------------------------------------------------------------------------------------------------------------|-----------------------------|
| Office of Naval Research<br>Attn: Code 472<br>800 North Quincy Street<br>Arlington, Virginia 22217                           | 2                           | U. S. Army Research Office<br>Attn: CRD-AA-IP<br>P.O. Box 1211<br>Research Triangle Park, N.C. 27709                                | 1                           |
| ONR Branch Office<br>Attn: Dr. George Sandoz<br>536 S. Clark Street<br>Chicago, Illinois 60605                               | 1                           | Naval Ocean Systems Center<br>Attn: Mr. Joe McCartney<br>San Diego, California 92152                                                | 1                           |
| ONR Branch Office<br>Attn: Scientific Dept.<br>715 Broadway<br>New York, New York 10003                                      | 1                           | Naval Weapons Center<br>Attn: Dr. A. B. Amster,<br>Chemistry Division<br>China Lake, California 93555                               | 1                           |
| ONR Branch Office<br>1030 East Green Street<br>Pasadena, California 91106                                                    | 1                           | Naval Civil Engineering Laboratory<br>Attn: Dr. R. W. Drisko<br>Port Hueneme, California 93401                                      | 1                           |
| ONR Branch Office<br>Attn: Dr. L. H. Peebles<br>Building 114, Section D<br>666 Summer Street<br>Boston, Massachusetts 02210  | 1                           | Department of Physics & Chemistry<br>Naval Postgraduate School<br>Monterey, California 93940                                        | 1                           |
| Director, Naval Research Laboratory<br>Attn: Code 6100<br>Washington, D.C. 20390                                             | 1                           | Dr. A. L. Slafkosky<br>Scientific Advisor<br>Commandant of the Marine Corps<br>(Code RD-1)<br>Washington, D.C. 20380                | 1                           |
| The Assistant Secretary<br>of the Navy (R,E&S)<br>Department of the Navy<br>Room 4E736, Pentagon<br>Washington, D.C. 20350   | 1                           | Office of Naval Research<br>Attn: Dr. Richard S. Miller<br>800 N. Quincy Street<br>Arlington, Virginia 22217                        | 1                           |
| Commander, Naval Air Systems Command<br>Attn: Code 310C (H. Rosenwasser)<br>Department of the Navy<br>Washington, D.C. 20360 | 1                           | Naval Ship Research and Development<br>Center<br>Attn: Dr. G. Bosmajian, Applied<br>Chemistry Division<br>Annapolis, Maryland 21401 | 1                           |
| Defense Documentation Center<br>Building 5, Cameron Station<br>Alexandria, Virginia 22314                                    | 12                          | Naval Ocean Systems Center<br>Attn: Dr. S. Yamamoto, Marine<br>Sciences Division<br>San Diego, California 91232                     | 1                           |
| Dr. Fred Saalfeld<br>Chemistry Division<br>Naval Research Laboratory<br>Washington, D.C. 20375                               | 1                           | Mr. John Boyle<br>Materials Branch<br>Naval Ship Engineering Center<br>Philadelphia, Pennsylvania 19112                             | 1                           |

# TECHNICAL REPORT DISTRIBUTION LIST, GEN

| No.                                                                                                                          | Copies |
|------------------------------------------------------------------------------------------------------------------------------|--------|
| Dr. Rudolph J. Marcus<br>Office of Naval Research<br>Scientific Liaison Group<br>American Embassy<br>APO San Francisco 96503 | 1      |
| Mr. James Kelley<br>DTNSRDC Code 2803<br>Annapolis, Maryland 21402                                                           | 1      |

# TECHNICAL REPORT DISTRIBUTION LIST, 356B

|                                                                                                                                  | <u>No.</u><br><u>Copies</u> |                                                                                                                                               | <u>No.</u><br><u>Copies</u> |
|----------------------------------------------------------------------------------------------------------------------------------|-----------------------------|-----------------------------------------------------------------------------------------------------------------------------------------------|-----------------------------|
| Dr. T. C. Williams<br>Union Carbide Corporation<br>Chemical and Plastics<br>Tarrytown Technical Center<br>Tarrytown, New York    | 1                           | Douglas Aircraft Company<br>3855 Lakewood Boulevard<br>Long Beach, California 90846<br>Attn: Technical Library<br>C1 290/36-84<br>AUTO-Sutton | 1                           |
| Dr. R. Soulen<br>Contract Research Department<br>Pennwalt Corporation<br>900 First Avenue<br>King of Prussia, Pennsylvania 19406 | 1                           | NASA-Lewis Research Center<br>21000 Brookpark Road<br>Cleveland, Ohio 44135<br>Attn: Dr. T. T. Serafini, MS 49-1                              | 1                           |
| Dr. A. G. MacDiarmid<br>University of Pennsylvania<br>Department of Chemistry<br>Philadelphia, Pennsylvania 19174                | 1                           | Dr. J. Griffith<br>Naval Research Laboratory<br>Chemistry Section, Code 6120<br>Washington, D.C. 20375                                        | 1                           |
| Dr. C. Pittman<br>University of Alabama<br>Department of Chemistry<br>University, Alabama 35486                                  | 1                           | Dr. G. Goodman<br>Globe-Union Incorporated<br>5757 North Green Bay Avenue<br>Milwaukee, Wisconsin 53201                                       | 1                           |
| Dr. H. Allcock<br>Pennsylvania State University<br>Department of Chemistry<br>University Park, Pennsylvania 16802                | 1                           | Dr. E. Fischer, Code 2853<br>Naval Ship Research and<br>Development Center<br>Annapolis Division<br>Annapolis, Maryland 21402                 | 1                           |
| Dr. M. Kenney<br>Case-Western University<br>Department of Chemistry<br>Cleveland, Ohio 44106                                     | 1                           | Dr. Martin H. Kaufman, Head<br>Materials Research Branch (Code 4542)<br>Naval Weapons Center<br>China Lake, California 93555                  | 1                           |
| Dr. R. Lenz<br>University of Massachusetts<br>Department of Chemistry<br>Amherst, Massachusetts 01002                            | 1                           | Dr. J. Magill<br>University of Pittsburg<br>Metallurgical and Materials<br>Engineering<br>Pittsburg, Pennsylvania 22230                       | 1                           |
| Dr. M. David Curtis<br>University of Michigan<br>Department of Chemistry<br>Ann Arbor, Michigan 48105                            | 1                           | Dr. D. Bergbreiter<br>Texas A&M University<br>Department of Chemistry<br>College Station, Texas 77843                                         | 1                           |
| Dr. M. Good<br>Division of Engineering Research<br>Louisiana State University<br>Baton Rouge, Louisiana 70803                    | 1                           | Professor R. Drago<br>Department of Chemistry<br>University of Illinois<br>Urbana, Illinois 61801                                             | 1                           |

# TECHNICAL REPORT DISTRIBUTION LIST, 356B

|                                                                                                                                                   | <u>No.</u><br><u>Copies</u> |
|---------------------------------------------------------------------------------------------------------------------------------------------------|-----------------------------|
| Dr. F. Brinkman<br>Chemical Stability & Corrosion<br>Division<br>Department of Commerce<br>National Bureau of Standards<br>Washington, D.C. 20234 | 1                           |
| Professor H. A. Titus<br>Department of Electrical Engineering<br>Naval Postgraduate School<br>Monterey, California 93940                          | 1                           |
| COL B. E. Clark, Code 100M<br>Office of Naval Research<br>800 N. Quincy Street<br>Arlington, Virginia 22217                                       | 1                           |
| Professor T. Katz<br>Department of Chemistry<br>Columbia University<br>New York, New York 10027                                                   | 1                           |
| Dr. E. Fischer, Code 1853<br>Naval Ship Research and<br>Development Center<br>Annapolis Division<br>Annapolis, Maryland 21403                     | 1                           |
| Dr. Martin E. Kaulman, Head<br>Naval Research Branch (Code 4242)<br>Naval Weapons Center<br>China Lake, California 93555                          | 1                           |
| Dr. J. Magill<br>University of Pittsburgh<br>Metallurgical and Materials<br>Engineering<br>Pittsburgh, Pennsylvania 15260                         | 1                           |
| Dr. D. Hargreaves<br>Texas A&M University<br>Department of Chemistry<br>College Station, Texas 77843                                              | 1                           |
| Professor R. Orsag<br>Department of Chemistry<br>University of Illinois<br>Urbana, Illinois 61801                                                 | 1                           |

|                                                                                                                               |   |
|-------------------------------------------------------------------------------------------------------------------------------|---|
| Dr. T. C. Williams<br>Union Carbide Corporation<br>Chemical and Plastics<br>Technical Center<br>Patterson, New York           | 1 |
| Dr. A. Socolin<br>Contract Research Department<br>General Electric<br>900 First Avenue<br>King of Prussia, Pennsylvania 19386 | 1 |
| Dr. A. C. Macdonald<br>University of Pennsylvania<br>Department of Chemistry<br>Philadelphia, Pennsylvania 19120              | 1 |
| Dr. C. Pittman<br>University of Alabama<br>Department of Chemistry<br>University, Alabama 35486                               | 1 |
| Dr. E. M. Minko<br>Pennsylvania State University<br>Department of Chemistry<br>University Park, Pennsylvania 16802            | 1 |
| Dr. M. Kanner<br>Case Western Reserve University<br>Department of Chemistry<br>Cleveland, Ohio 44106                          | 1 |
| Dr. E. Lenz<br>University of Massachusetts<br>Department of Chemistry<br>Amherst, Massachusetts 01003                         | 1 |
| Dr. M. David Curtis<br>University of Michigan<br>Department of Chemistry<br>Ann Arbor, Michigan 48106                         | 1 |
| Dr. M. Good<br>Division of Engineering Research<br>Louisiana State University<br>Baton Rouge, Louisiana 70803                 | 1 |